

U.S. PATENT APPLICATION

OF

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FOR

CHROMATOGRAPHY AND OTHER ADSORPTIONS  
USING MODIFIED CARBON CLAD METAL OXIDE PARTICLES

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## CHROMATOGRAPHY AND OTHER ADSORPTIONS USING MODIFIED CARBON CLAD METAL OXIDE PARTICLES

This application claims the benefit under 35 U.S.C. § 119(e) of prior U.S.  
5 Provisional Patent Application No. 60/229,696 filed September 1, 2000, which is  
incorporated in its entirety by reference herein.

### **FIELD OF THE INVENTION**

This invention relates to separation devices and processes as well as the use of certain  
10 modified carbonaceous materials as adsorbents and also relates to methods of using these  
adsorbents, including a method to increase the adsorption capacity and/or alter the adsorption  
affinity of carbonaceous materials capable of adsorbing an adsorbate.

### **BACKGROUND OF THE INVENTION**

15 Adsorption is an important operation in many industrial processes. The effectiveness  
of an adsorbent depends, primarily, on its surface area, pore structure, and surface chemistry.  
The nature of the adsorbate which is to be adsorbed frequently dictates the chemical nature  
of the adsorbent. For example, carbonaceous adsorbents are often used to selectively remove  
organic compounds from liquid, gaseous, or vapor media. Silica and alumina based  
20 adsorbents are employed to selectively adsorb polar adsorbates such as water, ammonia, and  
the like from similar media.

The efficacy of an adsorbent for a particular application is usually determined by the  
adsorption capacity and selectivity of the adsorbent for the adsorbate in question. The  
adsorption capacity may be measured per unit mass or per unit volume of the adsorbent. In  
25 general, the higher the adsorption capacity and selectivity of an adsorbent for a particular  
adsorbate, the more useful it is, since less of the adsorbent has to be used to effect the same  
removal of the adsorbate.

Carbonaceous materials, such as activated carbon, carbon black, and the like,  
represent an important class of adsorbents which are used in many fields such as separation,  
30 purification, and waste treatment, among others. Because of their widespread use, any  
method for improving the adsorption properties of carbonaceous adsorbents for a particular

adsorbate can have a large impact on the efficacy and economy of the processes utilizing them. Therefore, attempts have been made in the past to modify the surface chemistry of carbonaceous adsorbents. The methods employed for their modification can be broadly classified into physical and chemical means. In surface modification by physical means, a species is deposited on the surface of the carbonaceous adsorbent to form a layer which then changes its adsorption properties. However, such modification techniques have limited utility because the deposited layer is easily removed. In surface modification by chemical means, the modifying species is attached to the carbon surface by a chemical bonding mechanism.

10        The characteristics of the adsorption isotherm, representing the relationship between the extent of adsorption and adsorbate concentration or adsorbate partial pressure at a fixed temperature, is also of importance. As described by Sircar et al. in "Activated Carbon for Gas Separation and Storage," *Carbon*, Vol. 34, No. 1, pp. 1-12 (1996), the characteristics of the preferred adsorption isotherm will depend on the separation process being employed. For example, in cases where adsorbent regeneration is effected by a pressure swing, the preferred adsorbent is one with a moderate affinity for the adsorbate. When the adsorbate is strongly adsorbed, that is, when it has a strong affinity for the adsorbent, regeneration becomes difficult and energy intensive. On the other hand, when the adsorbent exhibits a weak affinity for the adsorbate, it has a small adsorption capacity at low adsorbent partial pressures and, hence, the adsorption mass transfer zone becomes very long. Thus, the availability of a method for altering the affinity of an adsorbent for an adsorbate is advantageous.

20        Thus, any method for increasing the adsorption capacity and/or modifying the adsorption affinity of the adsorbent enhances its usefulness in adsorption applications. As already noted, chemical modification can be used to alter the adsorptive properties of carbonaceous adsorbents. The range of chemical species which can be attached, however, is limited.

30        Bansal, Donnet and Stoeckli (in Chapter 5 of *Active Carbon*, Marcel Dekker, Inc., 1988) have reviewed different techniques of carbon surface modification. Physical impregnation methods are described, as are methods that rely on chemical reactions with various species to modify the surface of the carbon. Some of the chemical surface modification techniques described by Bansal et al. are oxidation, halogenation, sulfonation,

and ammoniation. Several of these techniques require treatment of the carbon at elevated temperatures. Another technique involving oxidation of the carbon with  $\text{HNO}_3$  in the presence of a catalyst, has been described by Sircar and Golden (U.S. Patent No. 4,702,749). However, these techniques have certain disadvantages apparent to those familiar with the field.

In chromatography and other separation methods, there is a certain amount of selectivity and efficiency that is necessary in order for the stationary phase to separate the various components in a mixture. For this reason, carbon products, such as carbon black, graphite, and activated carbon, have not been used as a standard stationary phase in certain separation systems because carbon is a strong non-specific adsorbent. This has been disappointing in the past, because carbon products, otherwise, would have many advantages over commercially available adsorbents. For instance, there are no corrosion problems with carbon products, which are stable at a wide pH range unlike silica particles which are stable only in the pH range of 1-8, nor are there any swelling problems with carbon products, which are stable in all organic solvents, unlike polysaccharide and/or polymer-based chromatographic particles, which have solvent restrictions. In addition, carbon products can be subjected to large temperature ranges and/or extreme pressures which would be beneficial for certain types of adsorptions, such as temperature swings used in some types of chromatography. In addition, with certain separation processes used in the production of biopharmaceuticals for clinical applications, the sterilization requirements or recommendations provide for the use of hot sodium hydroxide. With such sterilization procedures, the current popular stationary phases such as silica columns, cannot be used. Further, the polymeric columns such as cellulose polymers, are chemically but not physically stable to such sterilization treatments; in addition polymeric stationary phases are typically less efficient than metal oxide based stationary phases, resulting in poorer separations.

Accordingly, there is a need to provide a new class of adsorbents and new separation devices which can make use of carbon materials that have the advantages described above but are capable of being selective in their adsorption in order to serve as suitable adsorbents in separation processes such as chromatography.

## **SUMMARY OF THE INVENTION**

To achieve these and other advantages and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates to an adsorbent composition containing a modified carbonaceous material capable of adsorbing  
5 an adsorbate, wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group. Besides carbon-clad zirconium dioxide particles, other carbon-clad metal oxide particles can be used.

The present invention also relates to a separation device having a mobile phase and a stationary phase, wherein said stationary phase is a carbonaceous material having attached at  
10 least one organic group, wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group. The carbonaceous material having attached at least one organic group is capable of adsorbing one or more chemical species present in a mixture

The present invention further relates to a chromatography column containing a  
15 column having a stationary phase and a mobile phase. The stationary phase is at least a carbonaceous material having attached at least one organic group wherein the carbonaceous material having at least one organic group is capable of adsorbing at least one chemical species present in a mixture. The modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group.

20 The present invention further relates to a method for conducting chromatography on a substance and involves passing the substance through a column having a stationary phase and a mobile phase, wherein the stationary phase is at least a carbonaceous material having attached at least one organic group, and wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group. The  
25 chromatography can be, for instance, a size exclusion chromatography, an affinity-type chromatography, an adsorption-desorption chromatography, or variations thereof or combinations thereof. Also, the chromatography can be a reverse phase chromatography, ion exchange chromatography, supercritical fluid chromatography, hydrophobic interaction chromatography, or chiral chromatography.

30 The present invention, in addition, relates to bioseparations using the chromatography methods described above.

The present invention also relates to separations using electrophoresis wherein the stationary phase is a carbonaceous material having attached at least one organic group, wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group.

5       The present invention further relates to a separation device containing a membrane wherein said membrane contains a carbonaceous material having attached at least one organic group, wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group.

10       The separation device can also be a magnetic separation device or a reverse osmosis device wherein the stationary phase or the membrane contains a carbonaceous material having attached at least one organic group, wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group.

15       Another embodiment of the present invention relates to a method to increase the adsorption capacity of a carbonaceous material capable of adsorbing an adsorbate or altering the adsorption isotherm of the adsorbate on the adsorbent, for instance, to allow an easier regeneration of the adsorbent. In this method, at least one organic group capable of increasing the adsorption capacity of a carbonaceous material is attached to the carbonaceous material, wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group.

20       The present invention, in addition, relates to a method of adsorbing an adsorbate and includes the step of contacting the adsorbate with a carbonaceous material which has been modified by attaching an organic group. The modified carbonaceous material is capable of adsorbing the adsorbate and at least one organic group is attached to the carbonaceous material, wherein the modified carbonaceous material is carbon-clad zirconium dioxide particles having attached at least one organic group.

25       Additional features and advantages of the present invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the written description and appended claims.

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It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several embodiments of the present invention and together with the description, serve to explain the principles of the present invention.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figures 1-5 are various graphs plotting the separation of various analytes resulting from using various stationary phases of the present invention.

### **DETAILED DESCRIPTION OF THE PRESENT INVENTION**

The present invention relates to separation devices which typically have a stationary phase. The stationary phase, for purposes of the present invention, is carbon-clad zirconium dioxide particles having attached at least one organic group. This material is also known, once the organic group is attached, as modified carbon-clad zirconium dioxide particles for purposes of the present invention. For purposes of the present invention, the organic group is preferably attached (e.g., chemically) to the surfaces of the carbon-clad zirconium dioxide particles, preferably by covalent bonds. Other carbon-clad metal oxide(s) (but not including carbon clad silica) can be used in the present invention in lieu of, or in combination with, the carbon-clad zirconium dioxide. For exemplary purposes only, carbon-clad zirconium dioxide is discussed below with the understanding that other carbon-clad metal oxide(s) can be made and used in the same manner. Other examples include, but are not limited to, Group II, Group III, and Group IV metals. Specific examples include  $\text{HfO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{MgO}$ . For the purposes of this application, the term "metal oxide particles" does not include carbon-clad silica.

One preferred separation device is a chromatography column which, for purposes of the present invention, contains a column having a mobile phase and a stationary phase. The stationary phase is at least the modified carbon-clad zirconium dioxide particles of the present invention. The mobile phase can be any conventional mobile phase used in the separation of chemical compounds or species from a mixture, such as solvents and the like.

The present invention further relates to a method for conducting chromatography on a substance or mixture which involves passing the substance through a column packed with at least the modified carbon-clad zirconium dioxide particles as the stationary phase and the mobile phase. The type of chromatography that can be accomplished by the present invention includes, but is not limited to, size exclusion chromatography and affinity chromatography (wherein the affinity between the modified carbon-clad zirconium dioxide particles and the different chemical species in the mixture is different such that separation occurs at different rates). Another type of chromatography that can be accomplished by the present invention is adsorption-desorption chromatography, reverse phase chromatography, ion exchange chromatography, hydrophobic interaction chromatography, chiral chromatography, capillary liquid chromatography, supercritical fluid chromatography, or electrochromatography.

Chromatographic separation of proteins and other biomolecules can also be accomplished by the present invention. An example of such a bioseparation would involve the use of a stationary phase wherein polyols or polyethylene glycol compounds are attached on the carbon-clad zirconium dioxide particles. Another example of a bioseparation would involve the use of a stationary phase wherein benzoic acid or benzenesulfonic groups are attached to the surface of the carbon-clad zirconium dioxide particles.

Typically, a chromatographic system contains a mobile phase, a stationary phase, a pumping system, and a detector. Generally, the stationary phase contains insoluble particles which are preferably spherical and preferably range in size from about 1 micron to about 500 microns, and most preferably 2 to 5 microns, for analytical chromatography and 10 to 40 microns for preparative chromatographic applications. Also, these particles can have diameters of about 1 to about 2 mm or greater and/or with pore sizes of from 1 to about 2,000 Angstrom. These particles have a surface area ranging from about 1 to about 500 m<sup>2</sup>/g, preferably 15 to 100 m<sup>2</sup>/g, and a mean pore diameter ranging from about 20 to about 20,000 Angstrom, preferably 60 to 1000 Angstrom. The choice of these particles depends on the physical, chemical, and/or biological interactions that need to be exploited by the separation. Conventional stationary phases, such as silica, agarose, polystyrene-divinylbenzene, polyacrylamide, dextrin, hydroxyapatite, cross-linked polysaccharides, and polymethacrylates are functionalized with certain groups in order to accomplish the selective separation of particular chemical compounds from a mixture. The precise functional groups



that accomplish this desired specification are set forth, for instance, in Garcia, Bonen et al., "Bioseparation Process Science," Blackwell Science (1999), incorporated in its entirety by reference herein. In preferred instances, the functional groups described in Garcia et al. are the organic groups attached to the carbon-clad zirconium dioxide particles based on the present invention or are part of the organic groups attached to the carbon-clad zirconium dioxide particles (e.g., the functional groups of Garcia et al. attached to the carbon-clad zirconium dioxide particles through at least one aromatic group or alkyl group, wherein the aromatic group or alkyl group are preferably directly attached to the carbon-clad zirconium dioxide particles).

Another form of separation is electrophoresis which uses an applied electric field to produce directed movement of charged molecules. The process is similar to chromatographic methods in that a fixed barrier phase or stationary phase is used to facilitate separation. In the present invention, electrophoresis can be accomplished by using a stationary phase which contains the modified carbon-clad zirconium dioxide particles of the present invention.

Similarly, magnetic separations, such as magnetic bioseparations, can be accomplished using the modified magnetic carbon-clad zirconium dioxide particles of the present invention as the stationary phase.

In addition, membrane separations, such as reverse osmosis, can be accomplished by forming the membrane such that it contains modified carbon-clad zirconium dioxide particles. The membrane can be formed by dispersing the modified carbon-clad zirconium dioxide particles in a polymer and casting the polymer mixture to form a membrane. Another way to make the membrane is to form a conventional membrane and then surface modify the membrane to attached organic groups onto the membrane. Membranes can be used in a variety of separation techniques, including protein separations and/or metal removal.

Generally, any separation technique which involves the use of a stationary phase can be improved by the present invention. In particular, the stationary phase can be or can contain the modified carbon-clad zirconium dioxide particles of the present invention. Upon knowing the desired chemical compound or species to be separated, the modified carbon-clad zirconium dioxide particles can be tailored to be selective to the targeted chemical species by attaching an organic group or organic groups onto the carbon-clad zirconium dioxide particles to suit the separation needed. Since many functional groups are known to

cause particular selectivity in separations, these groups can be attached onto the carbon-clad zirconium dioxide particles to form the modified carbon-clad zirconium dioxide particles of the present invention and achieve the desired selectivity for separation processes.

5 In one embodiment, an adsorbent composition of the present invention contains a modified carbon-clad zirconium dioxide particles capable of adsorbing an adsorbate wherein at least one organic group is attached to the carbon-clad zirconium dioxide particles.

Preferred carbon-clad  $\text{ZrO}_2$  particles useful for the present invention comprise a porous core  $\text{ZrO}_2$  particle. The core preferably has a diameter of from 1 to 500 microns, more preferably about 2 to about 50 microns; a surface area of from about 5 to about 300  $\text{m}^2/\text{g}$ ,  
10 more preferably from about 15 to about 100  $\text{m}^2/\text{g}$ ; and a pore diameter of from about 20 to about 5000 Å, more preferably from about 60 to about 1000 Å.

The core  $\text{ZrO}_2$  particle has a cladding of carbon. As used herein, the phrase "carbon-clad" means that an outer layer, sheath, coating, or cladding of pyrolytic carbon is bonded or otherwise integrally attached to the underlying  $\text{ZrO}_2$  matrix. As used herein, "pyrolytic  
15 carbon" is intended to refer to carbon formed by the carbonization of a suitable carbon source, e.g., a hydrocarbon. "Carbonization" means that the hydrocarbon or other carbon source is subjected to conditions causing it to decompose into atomic carbon and other substances.

As mentioned above, the  $\text{ZrO}_2$  cores of the present carbon-clad particles are  
20 preferably porous. When discussing porosity, the term "open pores" refers to interior channels in the particles which exit at the surface of the particle. The term "closed pores" refers to pores which have no exit at the outside surface of the particle. The surface of closed pores are inaccessible to either gas or liquid phases with which the particles are contacted. Thus, the closed pores are not affected by the cladding process, nor do they participate in  
25 subsequent use of the particles in surface active applications. As used herein, the term "pores" (or "porosity") refers to "open pores" only. By "surface of the particle", it is meant the exterior surface as well as the surface of the open pores. It is intended that the carbon-cladding cover substantially all of the surface of the  $\text{ZrO}_2$  particle. As used herein, "substantially covering" or "substantially all" means that at least about 55%, preferably at  
30 least about 75%, and more preferably at least about 95% of the total surface area of the core  $\text{ZrO}_2$  particle is covered by the carbon-cladding.

Preferably, the thickness of the carbon-cladding over the surface of the  $\text{ZrO}_2$  core ranges from the diameter of a single carbon atom (a monatomic layer), to about 20 Å or more. This carbon-cladding will thus not appreciably increase the diameter of the  $\text{ZrO}_2$  particles. Thus, preferred carbon-clad  $\text{ZrO}_2$  particles of the present invention have a diameter  
5 of from about 1 to about 500 microns and more preferably from about 2 to about 50 microns. The carbon-clad  $\text{ZrO}_2$  particles preferably have an average pore diameter of from about 20 to about 5000 Å, more preferably from about 60 to about 1000 Å. The carbon-clad  $\text{ZrO}_2$  particles preferably have a surface area of from about 5 to about 300  $\text{m}^2/\text{g}$ , and more preferably from about 15 to about 100  $\text{m}^2/\text{g}$ .

10 The scope of the present invention is also intended to encompass carbon-clad  $\text{ZrO}_2$  particles which are essentially non-porous. Prior to carbon-cladding, preferred non-porous  $\text{ZrO}_2$  substrate particles have a diameter of from about 0.4 to about 7 microns, a surface area of from about 0.1 to about 3  $\text{m}^2/\text{g}$ , and negligible internal porosity, although the particles may have surface roughness. Useful non-porous  $\text{ZrO}_2$  having the preferred diameter and  
15 surface area values can be prepared by methods well known to those of ordinary skill in the art of ceramic powder preparation. The carbon-clad non-porous particles are believed to be particularly useful as a stationary phase support material in liquid chromatography separations of large molecules such as proteins and polymers. The size of such molecules can hinder or prohibit their rapid diffusion in and out of pores of a porous support material.

20 The carbon-clad particles of the present invention can also be combined with a suitable binder and used to coat a glass or plastic substrate to form plates for thin-layer chromatography. The carbon-clad zirconium particles that can be modified and used in the present invention are further described in U.S. Patent No. 5,108,997, which is incorporated in its entirety by reference herein. Also, the carbon-clad zirconium particles are commercially  
25 available from Zirchrom Inc.

The carbon-clad zirconium dioxide particles described above is then modified by the attachment of an organic group to the carbon-clad zirconium dioxide particles. Preferred processes for attaching an organic group to a carbon-clad zirconium dioxide particles and examples of organic groups are described in detail in U.S. Patent Nos. 5,554,739; 5,559,169;  
30 5,571,311; 5,575,845; 5,630,868; 5,672,198; 5,698,016; 5,837,045; 5,922,118; 5,968,243; 6,042,643; 5,900,029; 5,955,232; 5,895,522; 5,885,335; 5,851,280; 5,803,959; 5,713,988;

and 5,707,432; and International Patent Publication Nos. WO 97/47691; WO 99/23174; WO 99/31175; WO 99/51690; WO 99/63007; and WO 00/22051; all incorporated in their entirety by reference herein. These processes can be preferably used in preparing the modified carbon-clad zirconium dioxide particles of the present invention and permit the attachment of an organic group to the carbon-clad zirconium dioxide particles via a chemical reaction. As indicated above, the organic group attached to the carbon-clad zirconium dioxide particles is one preferably capable of increasing the adsorption capacity and/or selectivity of the carbon-clad zirconium dioxide particles and/or enhancing the resolution of solute peaks in chromatographic separations.

As indicated above, once the desired separation technique is chosen and the particular chemical species preferably known, a particular functional group or multiple functional groups can be chosen to be attached onto the carbon-clad zirconium dioxide particles in order to accomplish the selectivity needed to conduct the separation process. For instance, as set forth in Garcia et al., heparin is used in the separation of lipoproteins, accordingly, heparin can be attached onto carbon-clad zirconium dioxide particles in order to accomplish the desired separation. Similarly, when cationic exchange processes are needed, a sulfonic acid, for instance, can be attached on a carbon-clad zirconium dioxide particles and when anionic exchanges are needed, a quaternary amine can be attached onto the carbon-clad zirconium dioxide particles. Thus, with the present invention, and the knowledge possessed by one skilled in the art, separation techniques can be conducted using modified carbon-clad zirconium dioxide particles to achieve the selectivity desired.

Thus, the present invention provides modified carbon-clad zirconium dioxide particles which are resistant to corrosion, swelling, and/or extreme temperatures and pressures, but also provides the desired selectivity. In essence, the present invention gives the separation field the best of both worlds, namely, selectivity combined with a resilient stationary phase without any losses in the efficiency of separation.

A preferred process for attaching an organic group to the carbon-clad zirconium dioxide particles involves the reaction of at least one diazonium salt with carbon-clad zirconium dioxide particles in the absence of an externally applied current sufficient to reduce the diazonium salt. That is, the reaction between the diazonium salt and the carbon-clad zirconium dioxide particles proceeds without an external source of electrons sufficient

to reduce the diazonium salt. Mixtures of different diazonium salts may be used. This process can be carried out under a variety of reaction conditions and in any type of reaction medium, including both protic and aprotic solvent systems or slurries.

5 In another preferred process, at least one diazonium salt reacts with a carbon-clad zirconium dioxide particles in a protic reaction medium. Mixtures of different diazonium salts may be used in this process. This process can also be carried out under a variety of reaction conditions.

10 Preferably, in both processes, the diazonium salt is formed *in situ*. If desired, in either process, the modified carbon-clad zirconium dioxide particles can be isolated and dried by means known in the art. Furthermore, the modified carbon-clad zirconium dioxide particles can be treated to remove impurities by known techniques. The various preferred embodiments of these processes are discussed below.

15 The processes can be carried out under a wide variety of conditions and in general are not limited by any particular condition. The reaction conditions must be such that the particular diazonium salt is sufficiently stable to allow it to react with the carbon-clad zirconium dioxide particles. Thus, the processes can be carried out under reaction conditions where the diazonium salt is short lived. The reaction between the diazonium salt and the carbon-clad zirconium dioxide particles occurs, for example, over a wide range of pH and temperature. The processes can be carried out at acidic, neutral, and basic pH. Preferably,  
20 the pH ranges from about 1 to 9. The reaction temperature may preferably range from 0°C to 100°C.

Diazonium salts, as known in the art, may be formed for example by the reaction of primary amines with aqueous solutions of nitrous acid. A general discussion of diazonium salts and methods for their preparation is found in Morrison and Boyd, Organic Chemistry,  
25 5th Ed., pp. 973-983, (Allyn and Bacon, Inc. 1987) and March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structures, 4th Ed., (Wiley, 1992). According to this invention, a diazonium salt is an organic compound having one or more diazonium groups.

30 The diazonium salt may be prepared prior to reaction with the carbon-clad zirconium dioxide particles or, more preferably, generated *in situ* using techniques known in the art. *In situ* generation also allows the use of unstable diazonium salts such as alkyl diazonium salts

and avoids unnecessary handling or manipulation of the diazonium salt. In particularly preferred processes, both the nitrous acid and the diazonium salt are generated *in situ*.

A diazonium salt, as is known in the art, may be generated by reacting a primary amine, a nitrite and an acid. The nitrite may be any metal nitrite, preferably lithium nitrite, sodium nitrite, potassium nitrite, or zinc nitrite, or any organic nitrite such as for example isoamyl nitrite or ethyl nitrite. The acid may be any acid, inorganic or organic, which is effective in the generation of the diazonium salt. Preferred acids include nitric acid, HNO<sub>3</sub>, hydrochloric acid, HCl, and sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.

The diazonium salt may also be generated by reacting the primary amine with an aqueous solution of nitrogen dioxide. The aqueous solution of nitrogen dioxide, NO<sub>2</sub>/H<sub>2</sub>O, provides the nitrous acid needed to generate the diazonium salt.

Generating the diazonium salt in the presence of excess HCl may be less preferred than other alternatives because HCl is corrosive to stainless steel. Generation of the diazonium salt with NO<sub>2</sub>/H<sub>2</sub>O has the additional advantage of being less corrosive to stainless steel or other metals commonly used for reaction vessels. Generation using H<sub>2</sub>SO<sub>4</sub>/NaNO<sub>2</sub> or HNO<sub>3</sub>/NaNO<sub>2</sub> are also relatively non-corrosive.

In general, generating a diazonium salt from a primary amine, a nitrite, and an acid requires two equivalents of acid based on the amount of amine used. In an *in situ* process, the diazonium salt can be generated using one equivalent of the acid. When the primary amine contains a strong acid group, adding a separate acid may not be necessary. The acid group or groups of the primary amine can supply one or both of the needed equivalents of acid. When the primary amine contains a strong acid group, preferably either no additional acid or up to one equivalent of additional acid is added to a process of the invention to generate the diazonium salt *in situ*. A slight excess of additional acid may be used. One example of such a primary amine is para-aminobenzenesulfonic acid (sulfanilic acid).

In general, diazonium salts are thermally unstable. They are typically prepared in solution at low temperatures, such as 0-5°C, and used without isolation of the salt. Heating solutions of some diazonium salts may liberate nitrogen and form either the corresponding alcohols in acidic media or the organic free radicals in basic media.

However, the diazonium salt need only be sufficiently stable to allow reaction with the carbon-clad zirconium dioxide particles. Thus, the processes can be carried out with

some diazonium salts otherwise considered to be unstable and subject to decomposition. Some decomposition processes may compete with the reaction between the carbon-clad zirconium dioxide particles and the diazonium salt and may reduce the total number of organic groups attached to the carbon-clad zirconium dioxide particles. Further, the reaction may be carried out at elevated temperatures where many diazonium salts may be susceptible to decomposition. Elevated temperatures may also advantageously increase the solubility of the diazonium salt in the reaction medium and improve its handling during the process. However, elevated temperatures may result in some loss of the diazonium salt due to other decomposition processes.

Reagents can be added to form the diazonium salt *in situ*, to a suspension of carbon-clad zirconium dioxide particles in the reaction medium, *for example*, water. Thus, carbon-clad zirconium dioxide particle suspension to be used may already contain one or more reagents to generate the diazonium salt and the process accomplished by adding the remaining reagents.

Reactions to form a diazonium salt are compatible with a large variety of functional groups commonly found on organic compounds. Thus, only the availability of a diazonium salt for reaction with carbon-clad zirconium dioxide particles limits the processes of the invention.

The processes can be carried out in any reaction medium which allows the reaction between the diazonium salt and the carbon-clad zirconium dioxide particles to proceed. Preferably, the reaction medium is a solvent-based system. The solvent may be a protic solvent, an aprotic solvent, or a mixture of solvents. Protic solvents are solvents, like water or methanol, containing a hydrogen attached to an oxygen or nitrogen and thus are sufficiently acidic to form hydrogen bonds. Aprotic solvents are solvents which do not contain an acidic hydrogen as defined above. Aprotic solvents include, for example, solvents such as hexanes, tetrahydrofuran (THF), acetonitrile, and benzonitrile. For a discussion of protic and aprotic solvents see Morrison and Boyd, Organic Chemistry, 5<sup>th</sup> Ed., pp. 228-231, (Allyn and Bacon, Inc. 1987).

The processes are preferably carried out in a protic reaction medium, that is, in a protic solvent alone or a mixture of solvents which contains at least one protic solvent. Preferred protic media include, but are not limited to water, aqueous media containing water

and other solvents, alcohols, and any media containing an alcohol, or mixtures of such media.

The reaction between a diazonium salt and carbon-clad zirconium dioxide particles can take place with any type of carbon-clad zirconium dioxide particles, for example, in  
5 finely divided state or pelleted form. In one embodiment designed to reduce production costs, the reaction occurs during a process for forming carbon-clad zirconium dioxide particles pellets. For example, carbon-clad zirconium dioxide particles product of the invention can be prepared in a dry drum by spraying a solution or slurry of a diazonium salt onto carbon-clad zirconium dioxide particles. Alternatively, the carbon-clad zirconium  
10 dioxide particles can be prepared by palletizing carbon-clad zirconium dioxide particles in the presence of a solvent system, such as water, containing the diazonium salt or the reagents to generate the diazonium salt *in situ*. Aqueous solvent systems are preferred.

In general, the processes produce inorganic by-products, such as salts. In some end uses, such as those discussed below, these by-products may be undesirable. Several possible  
15 ways to produce carbon-clad zirconium dioxide particle products without unwanted inorganic by-products or salts are as follows:

First, the diazonium salt can be purified before use by removing the unwanted inorganic by-product using means known in the art. Second, the diazonium salt can be generated with the use of an organic nitrite as the diazotization agent yielding the  
20 corresponding alcohol rather than an inorganic salt. Third, when the diazonium salt is generated from an amine having an acid group and aqueous  $\text{NO}_2$ , no inorganic salts are formed. Other ways may be known to those of skill in the art.

In addition to the inorganic by-products, the process may also produce organic by-products. They can be removed, for example, by extraction with organic solvents. Other  
25 ways of obtaining products without unwarranted organic by-products may be known to those of skill in the art, and include washing or removal of ions by reverse osmosis.

The reaction between a diazonium salt and carbon-clad zirconium dioxide particles form carbon-clad zirconium dioxide particle products having an organic group attached to the carbon-clad zirconium dioxide particles. The diazonium salt may contain the organic  
30 group to be attached to the carbon-clad zirconium dioxide particles. It may be possible to



produce the carbon-clad zirconium dioxide particle products of this invention by other means known to those skilled in the art.

The organic group may be an aliphatic group, a cyclic organic group, or an organic compound having an aliphatic portion and a cyclic portion. As discussed above, the diazonium salt employed can be derived from a primary amine having one of these groups and being capable of forming, even transiently, a diazonium salt. The organic group may be substituted or unsubstituted, branched or unbranched. Aliphatic groups include, for example, groups derived from alkanes, alkenes, alcohols, ethers, aldehydes, ketones, carboxylic acids, and carbohydrates. Cyclic organic groups include, but are not limited to, alicyclic hydrocarbon groups (*for example*, cycloalkyls, cycloalkenyls), heterocyclic hydrocarbon groups (*for example*, pyrrolidinyl, pyrrolinyl, piperidinyl, morpholinyl, and the like), aryl groups (*for example*, phenyl, naphthyl, anthracenyl, and the like), and heteroaryl groups (imidazolyl, pyrazolyl, pyridinyl, thienyl, thiazolyl, furyl, indolyl, and the like). As the steric hindrance of a substituted organic group increases, the number of organic groups attached to the carbon-clad zirconium dioxide particles from the reaction between the diazonium salt and the carbon-clad zirconium dioxide particles may be diminished.

When the organic group is substituted, it may contain any functional group compatible with the formation of a diazonium salt. Functional groups include, but are not limited to, R, OR, COR, COOR, OCOR, carboxylate salts such as COOLi, COONa, COOK, COONR<sub>4</sub><sup>+</sup>, halogen, CN, NR<sub>2</sub>, SO<sub>3</sub>H, sulfonate salts such as SO<sub>3</sub>Li, SO<sub>3</sub>Na, SO<sub>3</sub>K, SO<sub>3</sub>NR<sub>4</sub><sup>+</sup>, OSO<sub>3</sub>H, OSO<sub>3</sub><sup>-</sup> salts, NR(COR), CONR<sub>2</sub>, NO<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, phosphonate salts such as PO<sub>3</sub>HNa and PO<sub>3</sub>Na<sub>2</sub>, phosphate salts such as OPO<sub>3</sub>HNa and OPO<sub>3</sub>Na<sub>2</sub>, N=NR, NR<sub>3</sub><sup>+</sup>X<sup>-</sup>, PR<sub>3</sub><sup>+</sup>X<sup>-</sup>, S<sub>k</sub>R, SSO<sub>3</sub>H, SSO<sub>3</sub><sup>-</sup> salts, SO<sub>2</sub>NRR', SO<sub>2</sub>SR, SNRR', SNQ, SO<sub>2</sub>NQ, CO<sub>2</sub>NQ, S-(1,4-piperazinediyl)-SR, 2-(1,3-dithianyl) 2-(1,3-dithiolanyl), SOR, and SO<sub>2</sub>R. R and R', which can be the same or different, are independently hydrogen, branched or unbranched C<sub>1</sub>-C<sub>20</sub> substituted or unsubstituted, saturated or unsaturated hydrocarbon, e.g., alkyl, alkenyl, alkynyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted arylalkyl. The integer k ranges from 1-8 and preferably from 2-4. The anion X<sup>-</sup> is a halide or an anion derived from a mineral or organic acid. Q is (CH<sub>2</sub>)<sub>w</sub>, (CH<sub>2</sub>)<sub>x</sub>O(CH<sub>2</sub>)<sub>z</sub>, (CH<sub>2</sub>)<sub>x</sub>NR(CH<sub>2</sub>)<sub>z</sub>, or (CH<sub>2</sub>)<sub>x</sub>S(CH<sub>2</sub>)<sub>z</sub>, where w is an integer from 2 to 6 and x and z are integers from 1 to 6. In the above formula,

specific examples of R and R' are  $\text{NH}_2\text{-C}_6\text{H}_4\text{-}$ ,  $\text{CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-NH}_2$ ,  $\text{CH}_2\text{-C}_6\text{H}_4\text{-NH}_2$ , and  $\text{C}_6\text{H}_5$ .

Another example of an organic group is an aromatic group of the formula  $\text{A}_y\text{Ar-}$ , which corresponds to a primary amine of the formula  $\text{A}_y\text{ArNH}_2$ . In this formula, the variables have the following meanings: Ar is an aromatic radical such as an aryl or heteroaryl group. Ar can be selected from the group consisting of phenyl, naphthyl, anthracenyl, phenanthrenyl, biphenyl, pyridinyl, benzothiadiazolyl, and benzothiazolyl; A is a substituent on the aromatic radical independently selected from a preferred functional group described above or A is a linear, branched or cyclic hydrocarbon radical (preferably containing 1 to 20 carbon atoms), unsubstituted or substituted with one or more of those functional groups; and y is an integer from 1 to the total number of  $\text{-CH}$  radicals in the aromatic radical. For instance, y is an integer from 1 to 5 when Ar is phenyl, 1 to 7 when Ar is naphthyl, 1 to 9 when Ar is anthracenyl, phenanthrenyl, or biphenyl, or 1 to 4 when Ar is pyridinyl.

Another set of organic groups which may be attached to the carbon-clad zirconium dioxide particles are organic groups substituted with an ionic or an ionizable group as a functional group. An ionizable group is one which is capable of forming an ionic group in the medium of use. The ionic group may be an anionic group or a cationic group and the ionizable group may form an anion or a cation.

Ionizable functional groups forming anions include, for example, acidic groups or salts of acidic groups. The organic groups, therefore, include groups derived from organic acids. Preferably, when it contains an ionizable group forming an anion, such an organic group has a) an aromatic group or a  $\text{C}_1\text{-C}_{12}$  alkyl group and b) at least one acidic group having a  $\text{pK}_a$  of less than 11, or at least one salt of an acidic group having a  $\text{pK}_a$  of less than 11, or a mixture of at least one acidic group having a  $\text{pK}_a$  of less than 11 and at least one salt of an acidic group having a  $\text{pK}_a$  of less than 11. The  $\text{pK}_a$  of the acidic group refers to the  $\text{pK}_a$  of the organic group as a whole, not just the acidic substituent. More preferably, the  $\text{pK}_a$  is less than 10 and most preferably less than 9. Preferably, the aromatic group or the  $\text{C}_1\text{-C}_{12}$  alkyl group of the organic group is directly attached to the carbon-clad zirconium dioxide particles. The aromatic group may be further substituted or unsubstituted, for example, with alkyl groups. The organic group can be a phenyl or a naphthyl group and the acidic group is a sulfonic acid group, a sulfinic acid group, a phosphonic acid group, or a carboxylic acid

group. The organic group may contain one or more asymmetric centers. Examples of these acidic groups and their salts are discussed above. The organic group can be a substituted or unsubstituted sulfophenyl group or a salt thereof; a substituted or unsubstituted (polysulfo)phenyl group or a salt thereof; a substituted or unsubstituted sulfonaphthyl group or a salt thereof; or a substituted or unsubstituted (polysulfo)naphthyl group or a salt thereof. An example of a substituted sulfophenyl group is hydroxysulfophenyl group or a salt thereof.

Specific organic groups having an ionizable functional group forming an anion (and their corresponding primary amines for use in a process according to the invention) are p-sulfophenyl (p-sulfanilic acid), 4-hydroxy-3-sulfophenyl (2-hydroxy-5-amino-benzenesulfonic acid), and 2-sulfoethyl (2-aminoethanesulfonic acid).

Amines represent examples of ionizable functional groups that form cationic groups. For example, amines may be protonated to form ammonium groups in acidic media. Preferably, an organic group having an amine substituent has a  $pK_b$  of less than 5. Quaternary ammonium groups ( $-NR_3^+$ ) and quaternary phosphonium groups ( $-PR_3^+$ ) also represent examples of cationic groups. The organic group can contain an aromatic group such as a phenyl or a naphthyl group and a quaternary ammonium or a quaternary phosphonium group. The aromatic group is preferably directly attached to the carbon-clad zirconium dioxide particles. Quaternized cyclic amines, and even quaternized aromatic amines, can also be used as the organic group. Thus, N-substituted pyridinium compounds, such as N-methyl-pyridyl, can be used in this regard. Examples of organic groups include, but are not limited to,  $(C_5H_4N)C_2H_5^+X^-$ ,  $C_6H_4(NC_5H_5)^+X^-$ ,  $C_6H_4COCH_2N(CH_3)_3^+X^-$ ,  $C_6H_4COCH_2(NC_5H_5)^+X^-$ ,  $(C_5H_4N)CH_3^+X^-$ , and  $C_6H_4CH_2N(CH_3)_3^+X^-$ , where  $X^-$  is a halide or an anion derived from a mineral or organic acid.

Aromatic sulfides encompass another group of organic groups. These aromatic sulfides can be represented by the formulas  $Ar(CH_2)_qS_k(CH_2)_rAr'$  or  $A-(CH_2)_qS_k(CH_2)_rAr''$  wherein  $Ar$  and  $Ar'$  are independently substituted or unsubstituted arylene or heteroarylene groups,  $Ar''$  is an aryl or heteroaryl group,  $k$  is 1 to 8 and  $q$  and  $r$  are 0-4. Substituted aryl groups would include substituted alkylaryl groups. Examples of arylene groups include phenylene groups, particularly p-phenylene groups, or benzothiazolylene groups. Aryl groups include phenyl, naphthyl and benzothiazolyl. The number of sulfurs present, defined

by k preferably ranges from 2 to 4. Examples of carbon-clad zirconium dioxide particles products are those having an attached aromatic sulfide organic group of the formula  $-(C_6H_4)-S_k-(C_6H_4)-$ , where k is an integer from 1 to 8, and more preferably where k ranges from 2 to 4. Other examples of aromatic sulfide groups are bis-para- $(C_6H_4)-S_2-(C_6H_4)-$  and para- $(C_6H_4)-S_2-(C_6H_5)-$ . The diazonium salts of these aromatic sulfide groups may be conveniently prepared from their corresponding primary amines,  $H_2N-Ar-S_k-Ar'-NH_2$  or  $H_2N-Ar-S_k-Ar''$ . Groups include dithiodi-4,1-phenylene, tetrathiodi-4,1-phenylene, phenyldithiophenylene, dithiodi-4,1-(3-chlorophenylene),  $-(4-C_6H_4)-S-S-(2-C_7H_4NS)$ ,  $-(4-C_6H_4)-S-S-(4-C_6H_4)-OH$ ,  $-6-(2-C_7H_3NS)-SH$ ,  $-(4-C_6H_4)-CH_2CH_2-S-S-CH_2CH_2-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-CH_2CH_2-S-S-S-CH_2CH_2-(4-C_6H_4)-$ ,  $-(2-C_6H_4)-S-S-(2-C_6H_4)-$ ,  $-(3-C_6H_4)-S-S-(3-C_6H_4)-$ ,  $-6-(C_6H_3N_2S)$ ,  $-6-(2-C_7H_3NS)-S-NRR'$  where  $RR'$  is  $-CH_2CH_2OCH_2CH_2-$ ,  $-(4-C_6H_4)-S-S-S-S-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-CH=CH_2$ ,  $-(4-C_6H_4)-S-SO_3H$ ,  $-(4-C_6H_4)-SO_2NH-(4-C_6H_4)-S-S-(4-C_6H_4)-NHSO_2-(4-C_6H_4)-$ ,  $-6-(2-C_7H_3NS)-S-S-2-(6-C_7H_3NS)-$ ,  $-(4-C_6H_4)-S-CH_2-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-SO_2-S-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-CH_2-S-CH_2-(4-C_6H_4)-$ ,  $-(3-C_6H_4)-CH_2-S-CH_2-(3-C_6H_4)-$ ,  $-(4-C_6H_4)-CH_2-S-S-CH_2-(4-C_6H_4)-$ ,  $-(3-C_6H_4)-CH_2-S-S-CH_2-(3-C_6H_4)-$ ,  $-(4-C_6H_4)-S-NRR'$ , where  $RR'$  is  $-CH_2CH_2OCH_2CH_2-$ ,  $-(4-C_6H_4)-SO_2NH-CH_2CH_2-S-S-CH_2CH_2-NHSO_2-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-2-(1,3-dithianyl)$ , and  $-(4-C_6H_4)-S-(1,4-piperizinediyl)-S-(4-C_6H_4)-$ .

Another set of organic groups which may be attached to the carbon-clad zirconium dioxide particles are organic groups having an aminophenyl, such as  $(C_6H_4)-NH_2$ ,  $(C_6H_4)-CH_2-(C_6H_4)-NH_2$ ,  $(C_6H_4)-SO_2-(C_6H_4)-NH_2$ .

Preferably, the organic group is a  $C_1-C_{100}$  alkyl group (more preferably a  $C_1-C_{12}$  alkyl group), an aromatic group, or other organic group, monomeric group, or polymeric group, each optionally having a functional group or ionic or ionizable group. More preferably, these groups are directly attached to the carbon-clad zirconium dioxide particles.

The polymeric group can be any polymeric group capable of being attached to a carbon product. The polymeric group can be a polyolefin group, a polystyrenic group, a polyacrylate group, a polyamide group, a polyester group, or mixtures thereof. Monomeric groups are monomeric versions of the polymeric groups.

The organic group can also be an olefin group, a styrenic group, an acrylate group, an amide group, an ester, or mixtures thereof. The organic group can also be an aromatic

group or an alkyl group, either group with an olefin group, a styrenic group, an acrylate group, an amide group, an ester group, or mixtures thereof, wherein preferably the aromatic group, or the alkyl group, like a C<sub>1</sub>-C<sub>12</sub> group, is directly attached to the carbon product.

5       The polymeric group can include an aromatic group or an alkyl group, like a C<sub>1</sub>-C<sub>12</sub> group, either group with a polyolefin group, a polystyrenic group, a polyacrylate group, a polyamide group, an polyester group, or mixtures thereof.

      The organic group can also comprise an aralkyl group or alkylaryl group, which is preferably directly attached to the carbon product. Other examples of organic groups  
10       include a C<sub>1</sub>-C<sub>100</sub> alkyl group, and more preferably a C<sub>20</sub>-C<sub>60</sub> alkyl group.

      Examples of other organic groups are organic groups having the following formulas (hyphens on one or more ends represents an attachment to a carbon product or to another group):

- Ar-CO<sub>2</sub>(C<sub>m</sub>H<sub>2m+1</sub>), where m = 0 to about 20;
- 15       -Ar-(C<sub>n</sub>H<sub>2n+1</sub>), where n = 1 to about 50;
- Ar-C<sub>p</sub>H<sub>2p</sub> Ar-, where p = 1 to about 10;
- Ar-CX<sub>3</sub>, where X is a halogen atom;
- Ar-O-CX<sub>3</sub>, where X is a halogen atom;
- Ar-SO<sub>3</sub><sup>-</sup>;
- 20       -Ar-SO<sub>2</sub>(C<sub>q</sub>H<sub>2q-1</sub>), where q = about 2 to about 10;
- Ar-S<sub>2</sub>-Ar-NH<sub>2</sub>;
- Ar-S<sub>2</sub>-Ar-;
- ArSO<sub>2</sub>H;
- Ar-((C<sub>n</sub>H<sub>2n</sub>)COOX)<sub>m</sub>, where n=0 to 20, m=1 to 3, and X=H, cations, or organic  
25       group; These groups are further activated and/or reacted with such groups as carbodiimides and further reacted with NH<sub>2</sub>-terminated functionalization groups; SOCl<sub>2</sub>, or PCl<sub>3</sub>, or PCl<sub>5</sub> to be converted to -Ar-(C<sub>n</sub>H<sub>2n</sub>)COCl)<sub>m</sub> groups and further reacted with OH-terminated functionalization groups.

      -Ar-((C<sub>n</sub>H<sub>2n</sub>)OH)<sub>m</sub>, where n=0 to 20, m=1 to 3; These groups are further activated  
30       and/or reacted with such groups as tosyl chloride and subsequently reacted with amino-

terminated ligands; carbonyldiimidazole and subsequently reacted with amino-terminated ligands; carbonylchloride terminated ligands; and epoxy terminated ligands.

-Ar-((C<sub>n</sub>H<sub>2n</sub>)NH<sub>2</sub>)<sub>m</sub>, where n=0 to 20, m=1 to 3, and its protonated form: -Ar-((C<sub>n</sub>H<sub>2n</sub>)NH<sub>3</sub>X)<sub>m</sub>, where X is an ion; These groups are further activated and/or reacted with  
5 such groups as carbodiimide activated carboxyl-terminated ligands; carbonyldiimidazole activated hydroxy-terminated ligands; tosyl activated hydroxy-terminated ligands; vinyl terminated ligands; alkylhalide terminated ligands; or epoxy terminated ligands.

-Ar-((C<sub>n</sub>H<sub>2n</sub>)CHNH<sub>3</sub><sup>+</sup>COO<sup>-</sup>)<sub>m</sub> where n=0 to 20 and m=1 to 3; These groups are derivatized further by reaction through the carboxylic group by reaction with NH<sub>2</sub> or OH  
10 terminated groups or through the amino group by reaction with activated carboxy-terminated ligands, activated hydroxy-terminated ligands, vinyl ligands, alkylhalide terminated ligands, or epoxy terminated ligands.

-Ar-((C<sub>n</sub>H<sub>2n</sub>)CH=CH<sub>2</sub>)<sub>m</sub>, where n=0 to 20, m=1 to 3 or -Ar-((C<sub>n</sub>H<sub>2n</sub>)SO<sub>2</sub>CH=CH<sub>2</sub>)<sub>m</sub>, where n=0 to 20, m=1 to 3. These groups are further activated  
15 and/or reacted with such groups as amino-terminated ligands; peroxy-acids to form epoxides and subsequently reacted with hydroxy- or amino-terminated ligands; hydrogen halides to form -Ar((C<sub>n</sub>H<sub>2n</sub>)CH<sub>2</sub>CH<sub>2</sub>X)<sub>m</sub> groups and subsequently reacted with amino-terminated ligands.

or mixtures thereof. Other reaction schemes can be used to form various groups  
20 onto the carbonaceous material.

Preferred mixtures of organic groups include the following:

- Ar-SO<sub>3</sub><sup>-</sup> and -Ar(C<sub>n</sub>H<sub>2n+1</sub>), where n = 1 to about 50;
- Ar-S<sub>2</sub>-Ar-NH<sub>2</sub> and -ArC<sub>p</sub>H<sub>2p</sub>Ar-, where p = 1 to about 10;
- Ar-S<sub>2</sub>-Ar- and -ArC<sub>p</sub>H<sub>2p</sub>Ar-, where p = 1 to about 10; or
- 25 at least two different -Ar-CO<sub>2</sub>(C<sub>m</sub>H<sub>2m+1</sub>), where m = 0 to about 20.

The various organic, monomeric, and polymeric groups described above and below which are part of the modified carbon product can be unsubstituted or substituted and can be branched or linear.

Any one or more of these organic groups, after attachment to the carbon-clad  
30 zirconium dioxide particles which permits adsorption, and preferably an increase in the

adsorption capacity of the carbon-clad zirconium dioxide particles may be used in the present invention.

Preferably, the organic group attached to the carbon-clad zirconium dioxide particles is an acid or base or a salt of an acid or base, and specific examples include phenyl or naphthyl groups having substituents like sulfonic acid and carboxylic acid. Quaternary ammonium can also be used. Most preferred organic groups attached to the carbon-clad zirconium dioxide particles are  $(C_6H_4)-SO_3^-Na^+$ ,  $(C_6H_4)-SO_3^-K^+$ ,  $(C_6H_4)-SO_3^-Li^+$ , and the like. Generally, an acid-type organic group attachment will be useful in adsorbing basic adsorbates while a base-type organic group attachment will be useful in adsorbing acidic adsorbates.

Other preferred organic groups which can be used in the present invention include amino acids and derivatized amino acids (e.g., phenyl alanine and its derivatives), cyclodextrins, immobilized proteins and polypeptides, and the like. Other organic groups include, but are not limited to,  $C_6F_5$ - groups and/or trifluoromethyl-phenyl groups, and bis-trifluorophenyl groups, other aromatic groups with fluorine groups, and the like. These organic groups are particularly preferred with respect to the embodiments of the present invention relating to chromatography and other separation techniques.

Other preferred organic groups which are attached onto the carbon-clad zirconium dioxide particles include  $-Ar-(C_nH_{2n+1})_x$  group functionalities, wherein n is an integer of from about 1 to about 30 and x is an integer of from about 1 to about 3, where n is preferably 8 or 18 and x is 1. These groups are particularly preferred for purposes of reverse phase chromatography. Another example of an organic group is benzene with a sulfonic group, benzoic groups, isophthalic groups which are particularly useful for cationic exchanges and quaternary amine groups which are particularly preferred for anionic exchanges.

Organic groups such as cyclodextrins which are directly attached onto the carbon-clad zirconium dioxide particles or attached through an alkyl group such as  $C_nH_{2n+1}$  chain wherein n is an integer of from about 3 to about 20 and also preferred. Other groups that can be attached are optically pure amino acids and derivatized amino acids, immobilized proteins, and the like. These types of organic groups are particularly preferred with respect to chiral chromatography.

In addition, polyethyleneglycol (PEG groups) and methoxy-terminated PEG groups as well as derivatized PEG and MPEG groups can be attached onto the carbon-clad zirconium dioxide particles. These types of organic groups are particularly preferred with respect to affinity and/or hydrophobic interactions chromatography for the separation, for instance, of proteins and polypeptides.

Additional examples of organic groups that can be attached alone or attached as an additional group onto the particles include  $-\text{Ar}-\text{C}(\text{CH}_3)_3$ ;  $-\text{Ar}-(\text{C}_n\text{H}_{2n})\text{CN}$  $_m$ , wherein Ar is an aromatic group, n is 0 to 20, and m is 1 to 3;  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{C}(\text{O})\text{N}(\text{H})-\text{C}_x\text{H}_{2x+1})_m$ , wherein Ar is an aromatic group, n is 0 to 20, x is 0 to 20 and m is 1 to 3;  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{N}(\text{H})\text{C}(\text{O})-\text{C}_x\text{H}_{2x+1})_m$ , wherein Ar is an aromatic group, n is 0 to 20, x is 0 to 20 and m is 1 to 3;  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{O}-\text{C}(\text{O})-\text{N}(\text{H})-\text{C}_x\text{H}_{2x+1})_m$ , wherein Ar is an aromatic group, n is 0 to 20, x is 0 to 20 and m is 1 to 3;  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{C}(\text{O})\text{N}(\text{H})-\text{R})_m$ , wherein Ar is an aromatic group, n is 0 to 20, x is 0 to 20 and m is 1 to 3, and R is an organic group;  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{N}(\text{H})\text{C}(\text{O})-\text{R})_m$ , wherein Ar is an aromatic group, n is 0 to 20, x is 0 to 20 and m is 1 to 3, and R is an organic group; and  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{O}-\text{C}(\text{O})\text{N}(\text{H})-\text{R})_m$ , wherein Ar is an aromatic group, n is 0 to 20, x is 0 to 20 and m is 1 to 3, and R is an organic group.

In addition, the present invention has the ability to attach organic groups such that the organic groups block out microporosity of the carbon-clad zirconium dioxide particles and thus permits the use of microporous materials for separation techniques, such as chromatography. Accordingly, the present invention permits the use of microporous materials that would otherwise not be chromatographically useful for separations.

In the present invention, more than one type of group can be attached onto the carbon-clad zirconium dioxide particles. This is especially useful to fill in any gaps on the surface of the carbon-clad zirconium dioxide particles not having an attached organic group. The filling in of such gaps promotes better selectivity and/or blocks any microporosity that may still exist in the carbon-clad zirconium dioxide particles. Typically, the optional second organic group is attached after the first primary organic group is attached and the modified carbon-clad zirconium dioxide particles is preferably purified as described above by removing any by-products that are produced from attaching an organic group onto the carbon-clad zirconium dioxide particles. Afterwards, the second organic group can then be



attached using the same diazonium salt or other attachment methods. Typically, the type of secondary organic groups which are subsequently attached include, but are not limited to, organic groups which are shorter in chain length or in steric hindrance. For instance, preferred secondary organic groups include, but are not limited to, phenyl groups, alkyl phenyl groups having short alkyl chains, and the like. Particularly preferred groups include, phenyl, methyl-phenyl, 3,5-dimethyl-phenyl, 4-isopropyl-phenyl, and 4-tert-butyl-phenyl.

The modified carbon-clad zirconium dioxide particles of the present invention, especially when the attached organic groups are alkyl phenyl groups, like 4-alkyl-phenyl, where the length of the alkyl chain is between 1 and 30, (preferably between 8 or 18), are especially useful for reverse phase chromatography applications having surface properties directly analogous to octadecyl-modified silica. Additionally, the modified carbon-clad zirconium dioxide particles described above, can have secondary attached groups such as phenyl, methyl-phenyl, dimethyl-phenyl, isopropyl-phenyl, tert-butyl-phenyl, and the like. The carbon-clad zirconium dioxide particles of the present invention will have one or more of the following properties compared to the conventional octadecyl silica:

- Enhanced pH stability (octadecyl silica is only used in a narrow pH and rarely above pH 8). The enhanced carbon-clad zirconium dioxide particles of the present invention will be stable at all pH.
- Enhanced temperature stability. These materials can be used at temperatures up to 250°C, preferably up to 200°C without significant degradation in performance.
- Enhanced resistance to swelling.
- Efficiency of separation comparable to silica and much greater than that of polymeric chromatographic materials.
- The ability to dial-in the surface properties by determining the concentration of active and endcapping groups on the surface, which would give the stationary phase different selectivities.

A combination of different organic groups is possible. For instance, it is within the bounds of the present invention to attach more than one type of organic group to the same carbon-clad zirconium dioxide particles or use a combination of carbon-clad zirconium dioxide particles, wherein some of the carbon-clad zirconium dioxide particles has been modified with one organic group and another portion of the carbon-clad zirconium dioxide

particles has been modified with a different organic group. Varying degrees of modification are also possible, such as low weight percent or surface area modification, or a high weight percent or surface area modification. Also, mixtures of modified carbon-clad zirconium dioxide particles and unmodified carbon-clad zirconium dioxide particles can be used.

5 Mixtures of modified carbon-clad zirconium dioxide particles with different functionalizations and/or different levels of treatment can be used.

Preferably, the modified carbon-clad zirconium dioxide particles of the present invention, especially when the attached organic group is a phenyl or naphthyl group having substituents like sulfonic acid, carboxylic acid, or quaternary ammonium or salts thereof, can  
10 be directly analogous to polymeric ion exchange resins. These types of carbon-clad zirconium dioxide particles of the present invention can have one or more of the following properties as compared to conventional polymeric ion exchangers:

- a) higher temperature stability;
- b) greater resistance to swelling; and
- 15 c) greater mechanical strength without adversely affecting uptake kinetics.

Furthermore, the modified carbon-clad zirconium dioxide particles of the present invention, besides being used as adsorbents, can also be used in separations ranging from water treatment to metals separation/recovery, ion exchange, catalysis, and the like. An additional advantage of an adsorbent possessing exchangeable groups as described above is  
20 that it confers on the material the ability to be further surface modified using ion exchange procedures.

With respect to the adsorbates, any adsorbate capable of being adsorbed by one or more of the modified carbon-clad zirconium dioxide particles of the present invention is contemplated to be within the bounds of the present invention. Examples include, but are  
25 not limited to, polar species such as water, ammonia, mercaptans, sulfur dioxide, and hydrogen sulfide. By "polar species," it is understood that this is a species whose electronic structure is not symmetrical. This includes molecules that possess dipole moments, for example  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ; and/or molecules that possess quadrupole moments, such as  $\text{CO}_2$  and molecules that possess unsaturated pi bonds ( $\pi$ ), such as alkenes, alkynes, and other organic  
30 and inorganic compounds with double and triple bonds. Non-polar species such as argon, oxygen, methane, and the like can also be adsorbed with the appropriate modified carbon-

clad zirconium dioxide particles of the present invention. In view of the description provided in this application, those skilled in the art will be able to determine which organic groups need to be attached to the carbon-clad zirconium dioxide particles in order to achieve the most effective adsorption affinity or increase in adsorption, depending upon the adsorbate and the adsorption processes involved.

By developing an adsorbent composition containing a modified carbon-clad zirconium dioxide particles capable of adsorbing an adsorbate, selectivity for a particular adsorbate can be enhanced. Using the proper modified carbon-clad zirconium dioxide particles, one can selectively adsorb particular species from a multicomponent mixture. In other words, modifying the carbon-clad zirconium dioxide particles to create the adsorbent composition of the present invention can decrease adsorption affinity for one component in order to maximize the adsorption affinity of another component which will maximize separation of the second component from the first component. Furthermore, by increasing adsorption of polar species, this further results in the relatively decreased adsorption of nonpolar species which improves selectivity. Further, the carbon-clad zirconium dioxide particles can be modified in such a manner as to add a hydrophobic group to "disable" the oxygen functionalities on the surface of the carbon-clad zirconium dioxide particles to increase the selectivity for the adsorption of nonpolar species.

The adsorbate can be in a liquid phase or in the gaseous or vapor phase, depending upon the needs and desires of the user. Certain adsorbates can be more efficiently adsorbed from the vapor or gaseous phases than from the liquid phase or vice versa, and the modified carbon-clad zirconium dioxide particles of the present invention are effective in adsorption from either phase.

One advantage of the present invention is to modify the surface of an activated carbon or carbon black adsorbent extensively, without damaging the structure or making the adsorbent more friable. For instance, carbon-clad zirconium dioxide particles can be surface modified based on the present invention with exchangeable sodium cations attached to the surface. This is very useful from the point of view of substituting different ions to alter the chemistry of the surface.

The beneficial effect of using the modified carbon-clad zirconium dioxide particles of the present invention for the purpose of adsorption can be demonstrated by comparing the

adsorption isotherms of an adsorbate on an unmodified carbonaceous adsorbent and the same carbonaceous adsorbent modified in accordance with the present invention.

The present invention will be further clarified by the following examples, which are intended to be purely exemplary of the present invention.

5 **EXAMPLES**

Example 1

Preparation of octadecylphenyl surface modified carbon-clad zirconia particles (SP-1)

15 g of deionized water and 15 g of ethanol, 0.83 g of 4-octadecylaniline and 1.01  
10 g of a 30 wt% nitric acid solution were mixed in a beaker and heated to 50 °C. 10 g of ZirChrom-Carb particles (provided by ZirChrom Separations, Anoka, MN) were added to the mixture and the temperature was increased to 60 °C. 0.83 g of a 20 wt% solution of sodium nitrite were added dropwise over 2 minutes. The mixture was left to react at 60 °C for 1.5 hours. After the reaction was complete, the reaction mixture was left to cool to  
15 room temperature and filtered using Whatman 1 filter paper. The particles were rinsed with ethanol, tetrahydrofuran (THF), and a 1 wt% NaOH solution and then soxhlet extracted for 16 hours in ethanol and 12 hours in THF. The particles SP-1 were subsequently left to dry. The starting particles ZirChrom-Carb particles had 1.18 wt% C and the final SP-1 particles had 3.4 wt%C, indicating surface coverage with  
20 octadecylphenyl groups.

Endcapping of octadecylphenyl surface modified carbon-clad zirconia particles with t-butylphenyl groups (SP-2)

The particles **SP-1** prepared in the previous step were mixed in a beaker with 22.5 g of deionized water, 7.5 g of ethanol, 0.22 g of 4-tert-butylaniline, and 0.63 g of a 30 wt%  
25 nitric acid solution and heated to 60 °C. 0.52 g of a 20 wt% solution of sodium nitrite were added dropwise over 2 minutes. The mixture was left to react at 60 °C for 1.5 hours. After the reaction was complete, the reaction mixture was left to cool to room temperature and filtered using Whatman 1 filter paper. The particles were rinsed with ethanol, THF, and 1 wt% NaOH solution and extracted in ethanol for 16 hours and THF for 8 hours. The  
30 particles SP-2 were subsequently left to dry. The final particles had 3.72 wt%C indicating that tert-butylphenyl groups were attached to the surface.

The particles **SP-2** were then slurry packed into a 50 x 4.6 mm HPLC column used in the subsequent examples of chromatographic separations.

### Example 2

#### Separation efficiency for 22 solutes

5        In order to demonstrate the chromatographic use of particles SP-2, the retention times of 22 solutes were measured. The solutes were injected in 5  $\mu$ l volumes into a mobile phase consisting of 40 vol% acetonitrile and 60 vol% water held at 30 °C and flowing at 1 ml/min. Table 1 contains the retention factors  $k'$  for these solutes for a column packed with the unmodified ZirChrom-Carb particles and for a column packed  
10        with particles SP-2. These retention factors were measured using a UV detector at 254 nm. Each solute has a different retention factor, which means that if a mixture of these solutes was injected into the column, they would elute at different times, enabling their separation. The effect of surface modification is seen in Table 1. The retention factors of all compounds in the column packed with SP-2 particles are different from those in the  
15        column packed with the unmodified ZirChrom-Carb particles. This indicates that a unique and different chromatographic selectivity was accomplished by surface modification.

20        Table 1. Retention factors ( $k'$ ) for 22 solutes obtained with a column packed with particles SP-2 compared to those of unmodified ZirChrom-Carb particles.

Solute	$k'$ ZirChrom- Carb	$k'$ (SP-2) C18/t-butyl
N-benzylformamide	0.49	0.222
Benzylalcohol	0.54	0.286
Phenol	0.59	0.236
3-phenylpropanol	1.19	0.488
p-chlorophenol	2.49	0.841
Acetophenone	2.06	1.057
Benzonitrile	1.55	1.012
Nitrobenzene	4.76	2.078
Methylbenzoate	3.75	1.884
Anisole	1.57	1.680
Benzene	0.76	1.454
p-chlorotoluene	5.79	6.919
p-nitrobenzyl chloride	13.90	4.604
Toluene	1.70	2.793
Benzophenone	16.91	6.512

Bromobenzene	3.57	5.097
Napthalene	39.48	18.046
Ethylbenzene	2.36	4.526
p-xylene	3.85	6.081
p-dichlorobenzene	8.50	10.159
Propylbenzene	4.73	8.332
Butylbenzene	9.12	15.393

### Example 3

Preparation of dodecylphenyl surface modified carbon-clad zirconia particles (SP-3) and t-butylphenyl endcapped dodecylphenyl surface modified carbon-clad zirconia particles (SP-4)

Dodecylphenyl surface modified carbon-clad zirconia particles (SP-3) were prepared using a similar procedure to that described in Example 1 for the preparation of particles SP-1, using equivalent molar amounts of 4-dodecylaniline instead of 4-octadecylaniline as the treating reagent. t-butyl phenyl endcapped dodecylphenyl surface modified carbon-clad zirconia particles (SP-4) were also prepared starting from particles SP-3, using a procedure similar to that described in Example 1 for the preparation of particles SP-2 from particles SP-1.

### Example 4

#### Effect of endcapping on the separation of pharmaceutical molecules

The retention of basic pharmaceutical molecules lidocaine, atenolol, and labetalol was measured using HPLC columns packed with ZirChrom-Carb, particles SP-2, SP-3, and SP-4. The solutes were injected in 5  $\mu$ l volumes into a mobile phase consisting of 80 vol% acetonitrile and 20 vol% 20 mM potassium phosphate buffer at pH 10, held at 30 °C and flowing at 1 ml/min. The retention factors are compared in Table 2. One observes that atenolol and labetalol are very strongly retained on the starting ZirChrom-Carb HPLC column, because their retention factors are greater than 30. Surface modification simply with a dodecylphenyl group (particles SP-3) decreases the retention factor for lidocaine, but does not effect the retention of atenolol and labetalol. It is only after endcapping with t-butylphenyl groups (particles SP-4 and SP-2) that the retention of atenolol and labetalol is significantly reduced. This reduction in retention indicates that adding the smaller t-butylphenyl groups helps improve the chromatographic performance by blocking access to the sites on the carbon surface responsible for the strong retention of these basic

pharmaceutical molecules.

**Table 2. Comparison of retention factors for basic pharmaceutical molecules on various HPLC columns packed with surface modified carbon-clad zirconia particles.**

Solute	k' ZirChrom-Carb	k' (SP-3) C12	k' (SP-4) C12/t-butyl	k' (SP-2) C18/t-butyl
Lidocaine	19.07	2.33	2.52	5.35
Atenolol	>30	>30	1.70	10.12
Labetalol	>30	>30	2.03	9.53

#### Example 5

##### Separation of barbiturates

A 5  $\mu$ l mixture of acetone, barbital, metharbital, butethal, hexobarbital, pentobarbital, and mephobarbital was introduced in a mobile phase consisting of 80 vol% acetonitrile, 20 vol% 20 mM Ammonium phosphate buffer at pH 7.0, flowing at 1 ml/min at 30 °C. The separation of analytes by an HPLC column packed with particles SP-2 is shown in Figure 1. The analytes were detected by UV absorption at 254 nm.

#### Example 6

##### The effect of temperature on the separation of PTH-aminoacids

In this example the effect of temperature on the separation of 3-phenyl-2-thiohydantoin (PTH) derivatized aminoacids is used to illustrate the advantages of performing chromatographic separations at higher temperatures using the column containing particles SP-2. A 1  $\mu$ l mixture of PTH derivatives of arginine, serine, glycine, alanine, isoaminobutyric acid, aminobutyric acid, valine, and norvaline was injected into a mobile phase consisting of 20 vol% Acetonitrile and 80 vol% of a 0.1 % trifluoroacetic acid solution at pH 2.0 with a flow rate of 1 ml/min. The separation is shown at 30 °C and 80 °C in Figure 2. Increasing the temperature by 50 °C reduces the separation time from greater than 14 minutes to less than 6 minutes, effectively halving the analysis time.

#### Example 7

##### Separation of nonsteroidal antiinflammatory drugs

The effect of temperature on the speed of chromatographic separations using the packing material SP-2 is also illustrated on this example of the separation of a mixture of acetaminophen, ketoprofen, ibuprofen, naproxen, and oxaprofen at 80 and 150 °C, which is shown in Figure 3. At 80 °C, an injection volume of 5 µl was used in combination with a gradient elution, with the mobile phase flowing at 1 ml/min and the composition transitioning over 20 minutes from 50 vol% to 80 vol% acetonitrile, and 50 vol% to 20 vol% 40 mM ammonium phosphate, 5mM ammonium at pH 2. At a temperature of 150 °C an injection volume of 1 µl was used with a mobile phase consisting of 75 vol% acetonitrile, and 25 vol% 40 mM phosphoric acid at pH 2.3 and a flow rate of 3.0 ml/min. The separation time dropped from approximately 3 minutes at 80 °C to less than 1 minute at 150 °C.

#### Example 8

##### Separation of ethylbenzene and p-xylene

The separation of these two molecules is very difficult using traditional silica based stationary phases. However, as is shown in Figure 4, a column packed with stationary phase SP-2 is capable of separating the mixture. An injection volume of 5 µl is used with a mobile phase consisting of 25 vol% acetonitrile, 25 vol% tetrahydrofuran, and 50 vol% water at 30 °C and a flowrate of 1 ml/min.

#### Example 9

##### Separation of beta-blockers

A column packed with SP-2 was used to separate a mixture of beta-blockers consisting of labetalol, metoprolol, and alprenolol. A 1 µl sample was injected into a mobile phase consisting of 45 vol% ACN and 55 vol% 20 mM ammonium phosphate at pH 11. The mobile phase was heated to 150 °C and flowing at a rate of 3 ml/min. The detection was by UV at 210 nm. As is shown in Figure 5, the separation was accomplished in less than 0.5 min.



Example 10

Preparation of benzenesulfonic acid surface modified carbon clad zirconia particles (SP-5)

11 g of deionized water and 4 g of ethanol, 0.17 g (1 mmol) of sulfanilic acid and  
5 0.21 g of a 30 wt% nitric acid solution (1 mmol) were mixed in a beaker and heated to 50  
°C. 5 g of ZirChrom-Carb particles were added to the mixture and the temperature was  
raised to 65 °C. 0.35 g of a 20 wt% solution of sodium nitrite (1 mmol) were added  
dropwise over 2 minutes. The mixture was left to react at 65 °C for 1.5 hours. After the  
reaction was complete, the reaction mixture was left to cool to room temperature and  
10 filtered using Whatman 1 filter paper. The particles were rinsed with deionized water,  
ethanol, methanol, and a 1 wt% NaOH solution and then extracted using the Dionex ASE-  
300 extractor with water, and a 50/50 ethanol-water mixture. The particles SP-5 were  
subsequently left to dry. The starting particles ZirChrom-Carb particles had 0.97 wt% C  
and the final SP-5 particles had 1.4 wt% C, indicating the attachment of benzenesulfonic  
15 groups.

Example 11

Preparation of phenyl ethylamide of dinitrobenzoyl-L-phenylglycine surface modified carbon clad zirconia particles (SP-6)

1.96 grams of dinitrobenzoyl-L-phenyl glycine [2, (4-aminophenyl) ethyl] amide  
20 were dissolved in a beaker containing a mixture of 31.5 ml tetrahydrofuran (THF) and 13.5  
ml deionized water and heated to 50 °C. 15 grams of Zirchrom-Carb were added and  
mixed for 5 minutes. 0.591ml of HCl was diluted with 1 ml of water and added to the  
reaction mixture. 0.256 grams of sodium nitrite was dissolved in 1 ml of water and added  
drop-wise to the reaction mixture. The reagents were mixed for 2 hours at 50 °C. The  
25 particles were filtered by vacuum filtration and washed with THF and Ethanol and  
subsequently extracted for 3 hours with THF. The starting particles ZirChrom-Carb  
particles had 1.68 wt% C and 0.05 wt% N and the final SP-6 particles had 3.1 wt% C and  
0.33 wt%N.

Example 12

Preparation of phenylethylamine surface modified carbon clad zirconia particles (SP-7)

45 g of deionized water and 20 g of ethanol, 0.72 g (5.3 mmol) of 4-aminophenethylamine and 1.93 g (10.6 mmol) of a 20 wt% hydrochloric acid solution were mixed in a beaker and heated to 40 °C. 22 g of ZirChrom-Carb particles were added to the mixture and the temperature was increased to 60 °C. 1.82 g (5.3 mmol) of a 20 wt% solution of sodium nitrite were added dropwise over 2 minutes. The mixture was left to react at 60 °C for 1.5 hours. After the reaction was complete, the reaction mixture was left to cool to room temperature and filtered using Whatman 1 filter paper. The particles were rinsed with ethanol, THF, and a 1 wt% NaOH solution and then soxhlet extracted overnight in ethanol. The particles SP-7 were subsequently left to dry. The starting ZirChrom-Carb particles had 1.03 wt% C and the final SP-7 particles had 2.41 wt%C, indicating surface coverage with phenethylamino groups.

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims or equivalents thereof.

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